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Oxacalix[3]arene-supported supertetrahedron**

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† Electronic supplementary information (ESI) available: Ac susceptibility studies. CCDC 890544. For ESI and crystallographic data in CIF or other electronic format see http://dx.doi.org/10.1039/C2CC34792J

Abstract

The initial use of oxacalix[3]arene in manganese chemistry affords an unusual [Mn_{10}] supertetrahedron with an even more unusual oxidation state distribution.

Introduction

Methylene-bridged calix[4]arenes have recently emerged as versatile bowl-shaped ligands for the construction of polynuclear metal cluster compounds.[1] Upon deprotonation, the polyphenolic lower-rim can be used as a scaffold to bind either transition or lanthanide metal centres (TM and LnM, respectively) which self-assemble to form elaborate molecules exhibiting fascinating structural and magnetic characteristics. The coordination chemistry of the thia-, sulfonyl- and sulfinylcalix[4]arenes has received significant attention;[2] these display markedly different metal binding properties to their methylene-bridged analogues due to the presence of additional donor atoms in the ligand framework. In stark contrast the coordination chemistry of the family of oxacalixarenes has been largely ignored; a search of the CCDC database for metal complexes of the oxacalixarene subunit (two phenols linked by an ethereal bridge) reveals 59 hits for a total of 8 ring sizes.[3] This is rather surprising when one considers the potential to subtly tune the nature of the metal binding site by controlled introduction of ≥ 1 ethereal bridge. For example, introduction of one bridge to the calix[4]arene framework produces a trapezoidal rather than square binding site as shown in Figure 1A. Furthermore, introduction of multiple ethereal bridges greatly expands the square binding site and may thus invoke coordination chemistry motifs akin to those of the thia-calix[4]arenes.

p-^{t}Bu-Homooxacalix[3]arene (TBOC[3], Fig. 1B) is a shallow bowl-shaped ligand that accounts for 23 of 59 hits in the abovementioned CCDC search. The majority of these hits are mononuclear complexes containing 4*f* or 5*f* elements, with only eight containing TM ions (Sc, V, Fe, Nb and Re).[4] Only one of the latter (a Nb_3(TBOC[3])$_3$ complex) contains more than two metal centres and none have been constructed for the investigation of their magnetic properties. Analysis of these complexes reveals that TBOC[3] displays high degrees of versatility in metal binding when in the bowl-conformation, in so far as up to all three ethereal oxygens can also coordinate to ions bound at the lower-rim. Bridging group coordination is a common feature in the presence of 4*f* and 5*f* ions,[4d-f,k] but is observed in just two cases for the TMs listed above.[4h] Conformational distortion is observed in the binding of Fe,[4l] Nb[4h] and Re ions,[4g] but the cone conformation is preserved in the formation of Sc and V complexes.[4b,i]

We have observed preferential binding of TM(III) rather than TM(II) ions in our study of manganese and iron coordination chemistry with calix[4]arene.[1b-e] Given that TBOC[3] presents a versatile

binding cavity, and that it differs markedly from calix[4]arene in terms of size and charge upon full deprotonation, we have begun to investigate the effect this will have on the prevailing coordination chemistry with manganese performed under benchtop conditions. Here we show that TBOC[3] is indeed capable of acting as a suitable support for cluster formation with manganese, that Mn(II) rather than Mn(III) is bound by the tris-phenolic pocket, and that these components self-assemble with additional Mn(II) and Mn(III) ions to form a [Mn_{10}] supertetrahedron with unusual oxidation state distribution.

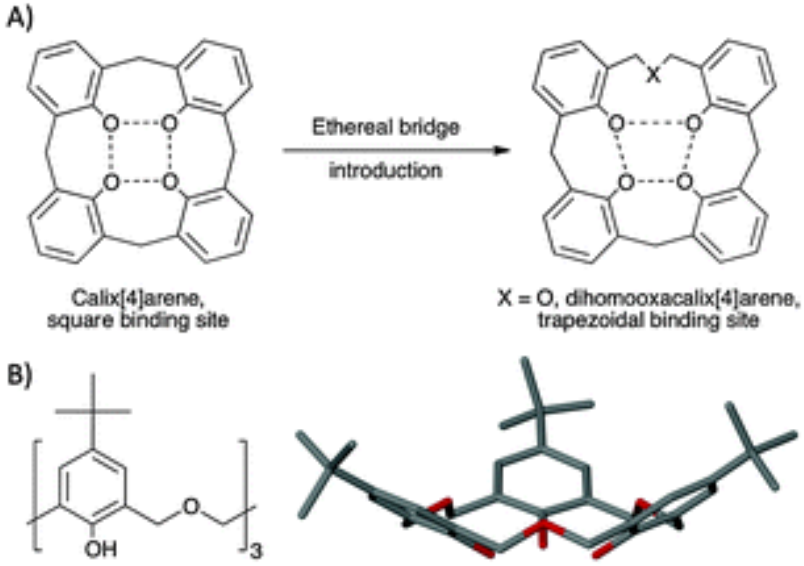


Figure 1. A) Schematic showing the change in the calix[4]arene metal binding site by introduction of one ethereal bridging group. B) Schematic and single crystal X-ray structure of *p*-^{t}Bu-homooxacalix[3]arene showing the shallow bowl conformation and position of ethereal O atoms. Solvent molecules and H atoms omitted for clarity.

During the course of our CCDC analysis we noted that the MeCN solvate of TBOC[3] was the only one reported to date.[4i] Examination of the extended structure of TBOC[3]·MeCN shows that the calixarenes stack one bowl on top of another to form columns, with MeCN crystallising in interstitial spaces. As we planned to carry out cluster forming reactions in DMF we crystallised TBOC[3] in order to observe related assembly behaviour. Crystals of TBOC[3]·DMF are in a trigonal cell and structure solution was performed in the space group *P*3.† To our surprise, structure analysis revealed that four molecules of TBOC[3] arrange at the vertices of a tetrahedron around a central DMF of crystallisation (Fig. 2 and S1). This assembly behaviour is markedly different to that observed in the acetonitrile solvate, and structure expansion shows that TBOC[3] cavities are occupied by ^{t}Bu groups from symmetry equivalent molecules.

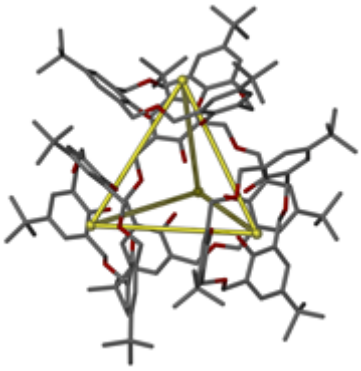


Figure 2. Extended structure TBOC[3]·DMF showing back-to-back calixarene packing. Solvent molecules and H atoms omitted for clarity.

The reaction of $MnCl_2 \cdot 4H_2O$, TBOC[3] and NEt_3 in a solvent mixture of DMF and EtOH followed by vapour diffusion with Et_2O, produces black crystals of **1** with formula $[Mn^{II}_6Mn^{III}_4O_4(TBOC[3])_4(Cl)_4(dmf)_3] \cdot 3.3H_2O \cdot 1.5$ dmf .‡ The crystals of **1** are in a monoclinic cell and structure solution was performed in the space group *C*2/*c*.† The metallic skeleton of **1** (Fig. 3 and 4) describes a mixed-valent $[Mn^{II}_6Mn^{III}_4]$ supertetrahedron. The six Mn(II) ions form two linear, perpendicular arrays: Mn9, Mn10 and Mn5 along the front horizontal edge, and Mn1, Mn3 and Mn7 along the back vertical edge, as drawn in Figure 3B. The cage is held together internally through the presence of four μ_4-O^{2-} ions (O25-O28) to afford a $[Mn_{10}O_4]^{16+}$ core that can also be regarded as four vertex-sharing $\{Mn^{III}_2Mn^{II}_2O\}^{8+}$ tetrahedra. The four μ_3-Cl^- ions (Cl1-Cl4), which themselves define a tetrahedron, each cap one face of the supertetrahedron, occupying the Jahn-Teller coordination sites on the Mn(III) ions (Mn2, Mn4, Mn6, Mn8). The fully deprotonated μ_4-TBOC[3] ligands cap each apex of the tetrahedron, using their three phenolate O-atoms to bond to the centrally housed Mn(II) ion and further bridge to the neighbouring Mn ions on the edges of the supertetrahedron. The Mn(III) ions are all six coordinate and in the axially-elongated octahedral $\{O_4Cl_2\}$ geometries expected for high spin d^4 ions. The Mn(II) ions are five coordinate and in distorted trigonal bipyramidal $\{O_5\}$ geometries, the remaining coordination site on each being occupied by a DMF molecule sitting in the cavity of the TBOC[3] ligand.

Interestingly the TBOC[3] ligands in complex **1** house Mn(II) ions in their polyphenolic pockets, and these “cluster ligands” then further bridge to Mn(III) ions. This is in complete contrast to all known calix[4]arene Mn clusters where the reverse is always true, the Mn(III) ions being housed within the ligand pocket with the Mn(II) ions located “externally”. The reason for this is somewhat unclear at present and will require the construction of a larger library of TBOC[3]-based complexes. However, we speculate that the more flexible polyphenolic pocket of TBOC[3] will more happily accommodate a larger ion with flexible geometry, in comparison to the rather rigid requirements of the smaller,

Jahn-Teller distorted Mn(III) ion. Indeed the TBC[4] ligand is perfectly set up to provide the four short equatorial bonds demanded by the Mn(III) ion. With only one related example it is only feasible to consider retention of the tetrahedral $(TBOC[3])_4$ unit coincidental, but it is an interesting possibility that such back-to-back calixarene packing may occur in other metal complexes.

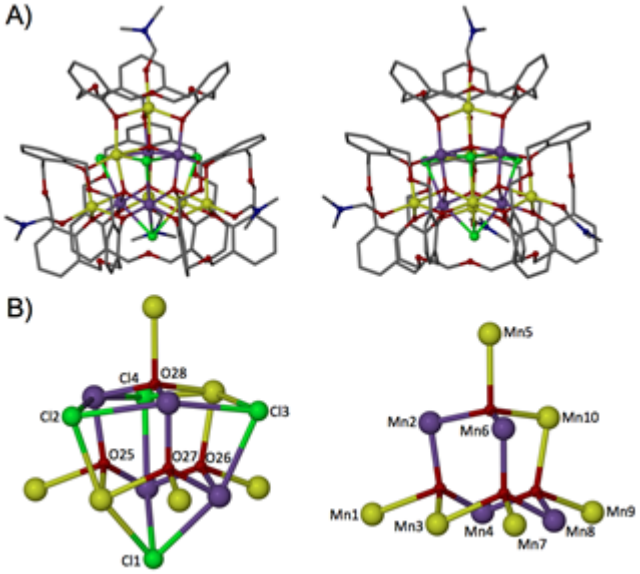
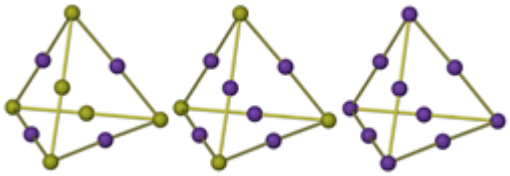


Figure 3. A) Orthogonal views of the molecular structure of complex **1**. B) The core of **1** with and without chloride ions. Colour code: Mn(III) = purple, Mn(II) = yellow, O = red, N = blue, C = black, Cl = green. *p*-^{t}Bu-groups and H-atoms have been omitted for clarity.

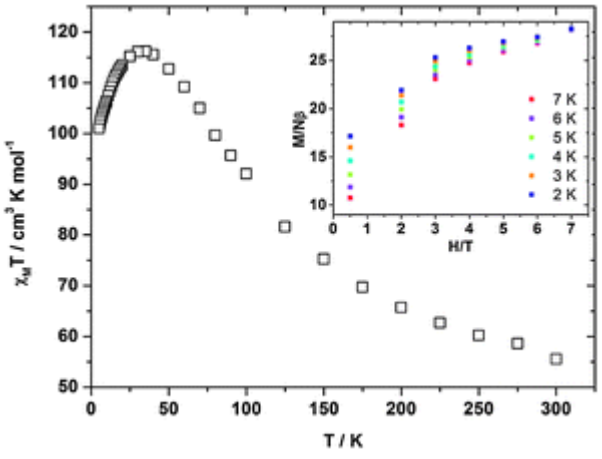
Complex **1** is only the sixth example of any polymetallic TM complex built with TBOC[3], the first example to contain more than two paramagnetic TM ions and the first Mn-based cluster of any kind. $[Mn_{10}]$ supertetrahedra are also rather uncommon; a CCDC search revealing only five previous examples.[5] Of these, three have a $[Mn^{III}_6Mn^{II}_4]$ oxidation state distribution, one contains only Mn(III) ions, and only the complex, $[Mn_{10}O_4(biphen)_4X_{12}]^{4-}$ (biphen = 2, 2'-biphenoxide; X = Cl^-, Br^-), has the $[Mn^{III}_4Mn^{II}_6]$ distribution seen in complex **1**. Figure 4 gives a pictorial comparison of the metallic skeletons of all known $[Mn_{10}]$ supertetrahedra.



← ***Figure 4.*** Comparison of the oxidation state distribution in published $[Mn_{10}]$ supertetrahedra. Mn(III) = purple, Mn(II) = yellow. $[Mn^{III}_4Mn^{II}_6]$ (left), $[Mn^{III}_6Mn^{II}_4]$ (middle) and $[Mn^{III}_{10}]$ (right).

Solid state dc magnetic susceptibility (χ_M) data on dried, polycrystalline **1** restrained in eicosane were collected in a 0.1 T magnetic field in the 5.0 - 300 K temperature range (Figure 5). The $\chi_M T$ product at 300 K is approximately 56 cm^3 K mol^{-1}, larger than that expected for a non-interacting $[Mn^{III}_4Mn^{II}_6]$ unit with g = 2.0 (38.25 cm^3 K mol^{-1}). As the temperature is decreased the $\chi_M T$ product increases, reaching a maximum value of ~116 cm^3 K mol^{-1} at 30 K. Below this temperature $\chi_M T$ drops to a value of ~101 cm^3 K mol^{-1} at 5 K. This behaviour is indicative of the presence of competing ferromagnetic and antiferromagnetic interactions, with the decrease of the $\chi_M T$ product at lower temperatures assigned to antiferromagnetic intermolecular interactions, zero-field splitting and/or Zeeman effects of the applied field. The presence of multilple Mn(II) ions, which often propagate weak exchange interactions, and the large nuclearity of the cluster likely results in a near continuum of energy levels and no isolated spin ground state. This picture is reflected in the magnetisation versus field data (inset of Figure 5) which shows M increasing only slowly with H, rather than quickly reaching saturation as one would expect for an isolated spin ground state. Accordingly the data could not be fitted satisfactorily with a simple model assuming only population of the ground spin state. Ac susceptibility studies in the 1.8-10.0 K range in a 3.5 G field oscillating at frequencies up to 1000 Hz (Fig. S2) display the tails of frequency-dependent out-of-phase (χ_M'') signals (suggestive of SMM behaviour) but no peaks. The behaviour of **1** in general is thus very similar to that observed for $[Mn_{10}O_4(biphen)_4X_{12}]^{4-}$.[6d]

For all reported $[Mn_{10}]$ supertetrahedra possessing the $[Mn^{III}_6Mn^{II}_4]$ oxidation state distribution (Figure 3a) - in which each neighbouring metal is in a different oxidation state - the pairwise magnetic exchange has been found to be ferromagnetic, with the molecules displaying isolated S = 22 ground states.[6] For the sole $[Mn^{III}_{10}]$ cluster the ground state is likely S = 0.[6c] Complex **1** and $[Mn_{10}O_4(biphen)_4X_{12}]^{4-}$, which contain both Mn(II)-Mn(III) and Mn(II)-Mn(II) nearest neighbours along the edges of their tetrahedra are, perhaps not surprisingly, appear to have ground state spin values intermediate between the two.



←***Figure 5.*** Plot of $\chi_M T$ versus T for complex **1** in an applied field of 0.1T. Inset: Plot of magnetisation versus field at the indicated temperatures and fields.

Conclusions

We have shown that TBOC[3] is a promising ligand for the assembly of coordination clusters that have interesting magnetic properties. Exploratory manganese chemistry has afforded a supertetrahedron with unusual oxidation state distribution, suggesting that other interesting clusters may be isolated with different TMs. Versatility in the calixarene conformation may also prove useful in the isolation of new polynuclear lanthanide species. The goals will be the focus of future work.

Notes and references

‡ TBOC[3] was prepared according to a literature procedure.[7] $MnCl_2 \cdot 4H_2O$ (0.1g, 0.5 mmol), TBOC[3] (0.1g, 0.17 mmol), NH_4ClO_4 (0.06g, 0.5 mmol) and NEt_3 (0.02g, 2 mmol) were added to a solvent mixture of MeCN (10ml) and DMF (10 ml) and stirred for 2 hours. Filtration of the solution followed by hexane diffusion afforded brown crystals of **1** in ~40% yield after 3 days. Elemental analysis (%), calculated (found): C 55.91 (56.24), H 6.34 (6.43), N 2.05 (2.04). **General Crystallographic Details:** Single crystal X-ray diffraction data were collected on a Bruker Apex II CCD Diffractometer operating at 100(2) K wtih MoKα radiation (λ = 0.71073 Å). **Crystal data for TBOC[3]·DMF:** $C_{153}H_{213}N_3O_{27}$, M = 2526.26, Colourless Block, 0.30 × 0.20 × 0.15 mm^3, trigonal, space group $P3$ (No. 143), $a = b$ = 16.5740(7), c = 15.5660(8) Å, V = 3703.1(3) $Å^3$, Z = 1, $2\theta_{max}$ = 53.4º, 22249 reflections collected, 8453 unique (R_{int} = 0.0316). Final *GooF* = 0.899, *R1* = 0.0601, *wR2* = 0.1450, *R* indices based on 5399 reflections with I >2sigma(I) (refinement on F^2). **Crystal data for 1:** $C_{160.50}H_{225.10}Cl_4Mn_{10}N_{5.50}O_{36.80}$, M = 3511.56, Brown Block, 0.40 × 0.30 × 0.25 mm^3, monoclinic, space group $C2/c$ (No. 15), a = 37.8284(18), b = 27.8091(13), c = 37.6849(19) Å, β = 114.965(2)°, V = 35939(3) $Å^3$, Z = 8, $2\theta_{max}$ = 51.4º, 133789 reflections collected, 33987 unique (R_{int} = 0.1410). Final *GooF* = 1.236, *R1* = 0.1056, *wR2* = 0.2373, *R* indices based on 13217 reflections with I >2sigma(I) (refinement on F^2).

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